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Review Article

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Recent progress in direct urea fuel cell

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Abstract: Direct urea fuel cell (DUFC) has attracted many researchers' attention due to the use of wastewater, for example urine, which contains urea for the fuel. The main factor to improve the electrochemical oxidation performance of urea and further enhance the performances of DUFC is the use of a good anode catalyst. Non-noble metal catalyst, such as nickel, is reported to have a good catalytic activity in alkaline medium towards urea electro-oxidation. Besides optimizing the anode catalyst, the use of supporting electrode which has a large surface area as well as the use of H_2O_2 as an oxidant to replace O_2 could help to improve the performances. The recent progress in anode catalysts for DUFC is overviewed in this article. In addition, the advantages and disadvantages as well as the factors that could help to escalate the performance of DUFC are discussed together with the challenges and future perspectives.

Keywords: fuel cell, urea, electro-oxidation, anode catalyst

1 Introduction

Global energy demands keep increasing every year, while most energy sources are still depending on fossil fuels [1]. Accordingly, other alternatives of the clean, environmentally safe, and low cost energy sources are necessary to be developed [2–7]. The use of wastewater as an alternative source of energy has obtained great attentions due to at least two problems, energy demand and wastewater treatment, which can be solved. One of the challenging efforts is the application of urine as a fuel in direct urea fuel cells (DUFCs). Urea, widely found in wastewater, is an organic compound containing carbon, hydrogen, and oxygen. The amount of hydrogen in urea is around 6.67 wt%. Therefore, urea, which is found around 2–2.5 wt% in the wastewater (urine), is classified as an acceptable source for DUFC in alkaline medium [1,8–10]. As an energy source, urea has some good characteristics, such as having a high energy density (16.9 MJ L^{-1}) that is ten times higher than hydrogen, safe and acceptable in transportation as well as non-flammable and non-toxic [11–13].

On the other hand, fuel cell is a device which electrochemically transforms fuel energy into electricity with high efficiency [14–16]. Many types of fuel cells have been reported. Besides proton exchange membrane fuel cell (PEMFC), which is the most popular one [17,18], there are also other types of fuel cells, including solid oxide fuel cell (SOFC) [19–21], molten carbonate fuel cell (MCFC) [22,23], alkaline fuel cell [24–26], and urea fuel cells. DUFC is an encouraging and effective method for energy production with urea, urine, and wastewater as the fuels [27]. In this system, urea or urine is electrochemically oxidized to produce CO_2, N_2, and H_2O and electricity. Oxygen is necessary to perform the oxidation reactions. The reactions occurring in DUFC are mentioned below [28]:

$$\begin{aligned}&\text{Anode: } CO(NH_2)_2 + 6OH^- \rightarrow CO_2 + N_2 + 5H_2O + 6e^-,\\ &E^0 = -0.746\ \text{V(vs standard hydrogen electrode (SHE))},\end{aligned} \tag{1}$$

$$\begin{aligned}&\text{Cathode: } O_2 + 2H_2O + 4e^- \rightarrow 4OH^-,\\ &E^0 = -0.40\ \text{V(vs SHE)},\end{aligned} \tag{2}$$

$$\begin{aligned}&\text{Overall: } 2CO(NH_2)_2 + 3O_2 \rightarrow 2CO_2 + 2N_2 + 4H_2O,\\ &E^0 = -1.146\ \text{V(vs SHE)},\end{aligned} \tag{3}$$

It is also known that H_2O_2 can be used as the alternative of O as it can provide a higher electrode potential, around two times higher, than the use of O_2 in alkaline medium [29]. Furthermore, the direct urea/H_2O_2 fuel cell has a more compact design, since urea and H_2O_2 are in the aqueous forms [30]. The reaction occurred is quite similar with the use of H_2O_2 at the cathode as the exception, and therefore gives an impact to the overall reactions.

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$$\text{Cathode: } 3H_2O_2 + 6H^+ + 6e^- \rightarrow 6H_2O,\quad E^0 = 1.763\ \text{V(vs SHE)}, \tag{4}$$

$$\text{Overall: } CO(NH_2)_2 + 3H_2O_2 + 6H^+ + 8OH^- \rightarrow CO_3^{2-} + N_2 + 12H_2O,\quad E^0 = -0.40\ \text{V(vs SHE)}, \tag{5}$$

Figure 1 shows the typical schematic diagram of DUFCs. At the cathode catalyst, electrochemical reduction reaction of O_2 or H_2O_2 in the cathode chamber produces OH^- ions, which then transport through the anion exchange membrane to reach the anode chamber. In this chamber, the OH^- ions react with urea and release electrons, which are later transferred to the cathode over the external circuit to produce electricity [28].

Research about the use of urea to generate electricity was initiated in 1973 using Pt as the electrodes for both anode and cathode with an anion exchange membrane to separate the anode and cathode chambers [31]. The investigation concluded that urea could be oxidized into CO_2, N_2, and H_2O, but needs further development. In 2010, Lan et al. examined DUFCs with urea as well as urine and AdBlue (32.5% urea aqueous solution) as the fuels [10]. Comparison between Pt and Ni/C as the anode was performed with Ag/C and MnO_2/C used as the cathode. A maximum power density of 1.7 mW cm^{-2} was obtained at 50°C operation at Ni/C and MnO_2/C as the anode and cathode, respectively, with 1 M solution of urea as the fuel. Until now, the development of anode catalyst for DUFCs has been investigated to maximize the power density of DUFCs. Many catalysts, including noble and non-noble metals have been examined to enhance the performance of this type of fuel cell.

This report summarized about recent development in DUFC, particularly the use of supporting anode catalysts and their influences on the DUFC performances. The explanation on advantages and disadvantages as well as the strategy to fabricate better catalysts were also elaborated. In addition, the influences of the external factors as well as the challenges and future prospects are also investigated to maximize the performances.

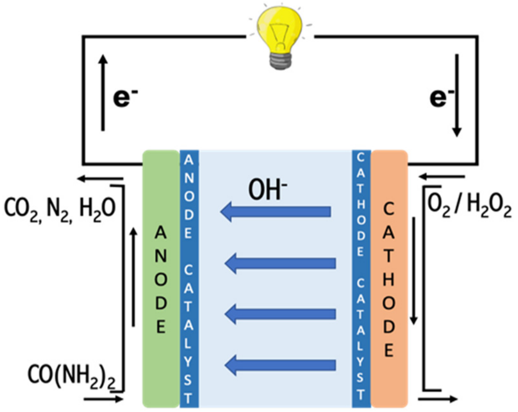

Figure 1: Schematic diagram of DUFC.

2 Mechanism of urea electro-oxidation

Urea could be oxidized either in alkaline, neutral, or acidic medium with N_2 and CO_2 as the products. However, there are some differences in the products and intermediate products reaction in different pH supporting electrolytes.

2.1 Neutral medium mechanism

In neutral medium, for example NaCl solution as the electrolyte, Cl^- is oxidized into Cl_2 which is disproportionated in aqueous solution to form HOCl. HOCl will be reduced back to Cl^-, while urea is electro-oxidized according to the following reactions [32]:

$$6Cl^- \rightarrow 3Cl_2 + 6e^-, \tag{6}$$

$$3Cl_2 + 3H_2O \rightarrow 3HOCl + 3H^+ + 3Cl^- \tag{7}$$

$$3HOCl + 3CO(NH_2)_2 \rightarrow N_2 + CO_2 + 3H^+ + 3Cl^- + 2H_2O, \tag{8}$$

$$\text{Overall reactions: } CO(NH_2)_2 + H_2O \rightarrow N_2 + CO_2 + 6H^+ + 6e^-. \tag{9}$$

H^+ is generated in this condition, hence, catalyst which has a resistance against acid is needed as the anode catalyst, such as RuO_2 and IrO_2 [12,32]. It was reported that urea was successfully oxidized to CO_2 and N_2 by using RuO_2–TiO_2-coated titanium electrode [32].

2.2 Alkaline medium mechanism

Under alkaline medium, urea is electro-oxidized at a lower cost by using Ni as the catalyst [33,34]. Moreover, it is reported that the use of Ni metal, nickel hydroxides, or Ni composites as the catalyst resulted in a better performance toward urea electro-oxidation than using other noble metal catalysts, such as Pt, Pt–Ir, etc., [35]. Lower oxidation potentials and higher current densities could be obtained.

Suarez et al. [36] proposed that the active sites of urea's dissociation process are Ni and hydroxide groups. The urea molecule is bound with two Ni sites, one Ni binds to the O of urea, while the other is linked to one of the amine groups. The bridge formed by the hydroxide group has been studied to be involved in this reaction to devote a proton to the amine group that connected to the Ni site.

Ni is an active element. In humid air, Ni is easily oxidized into NiO and $Ni(OH)_2$ will be further oxidized to NiOOH during the cyclic voltammetry treatment in alkaline medium [37,38]. NiOOH is known as the active catalyst for electrochemical oxidation of urea. The oxidation process occurred according to the following reactions:

$$Ni_{(metal)} + H_2O \rightarrow (NiOH)_{ad} + H^+ + e^-, \quad (10)$$

$$(NiOH)_{ad} + H_2O \rightarrow (NiOH \cdot H_2O)_{ad} \quad (11)$$

$$(NiOH \cdot H_2O)_{ad} \rightarrow Ni(OH)_2 + H^+ + e^-, \quad (12)$$

$$Ni + 2OH^- \rightarrow Ni(OH)_2 + 2e^- \quad (13)$$

$$Ni(OH)_{2(s)} + OH^- \rightarrow NiOOH + H_2O + e^-. \quad (14)$$

$Ni(OH)_2$ is generally formed in two crystallographic species, α-$Ni(OH)_2$ (Figure 2a) and β-$Ni(OH)_2$ (Figure 2b). The form of β-$Ni(OH)_2$ is more stable due to its Ni octahedral structure coordination with eight O atoms. Meanwhile, the α-$Ni(OH)_2$ form is less stable due to the presence of water molecules intercalated between the NiO_2 layers. β-$Ni(OH)_2$ could be formed by potential cycling in alkaline medium and by increasing the potential [39], whereas at the higher potential, γ-$Ni(OH)_2$ is formed and can be reduced back to β-$Ni(OH)_2$ in the reverse scan [40,41].

Electro-oxidation of urea by Ni catalyst in alkaline medium is proposed to occur in two possible mechanisms, including:

2.2.1 Indirect mechanism

The common mechanism used to explain the urea electro-oxidation is indirect mechanism with NiOOH as the active catalyst for electro-oxidation of urea. NiOOH formed from the electro-oxidation of $Ni(OH)_2$ oxidizes the urea molecules and is reduced back to $Ni(OH)_2$ according to the following equations [42]:

$$6Ni(OH)_{2(s)} + 6OH^- \rightarrow 6NiOOH + H_2O + 6e^-, \quad (15)$$

$$6NiOOH_{(s)} + CO(NH_2)_{2(aq)} + H_2O_{(l)} \rightarrow 6Ni(OH)_{2(s)} + N_{2(g)} + CO_{2(g)}, \quad (16)$$

Overall reaction:

$$CO(NH_2)_{2(aq)} + 6OH^- \rightarrow N_{2(g)} + 5H_2O_{(l)} + CO_{2(g)} + 6e^-, \quad (17)$$

2.2.2 Direct mechanism

In the direct mechanism, urea is oxidized by Ni in the form of NiOOH which is not reduced back to the Ni$(OH)_2$ form. The oxidation process will use OH^- and the NiOOH will be reduced at the reverse scan [43]. According to Guo et al., the proposed direct mechanisms are the following reactions [43]:

$$Ni(OH)_2 + OH^- \rightleftharpoons NiOOH + H_2O + e^-, \quad (18)$$

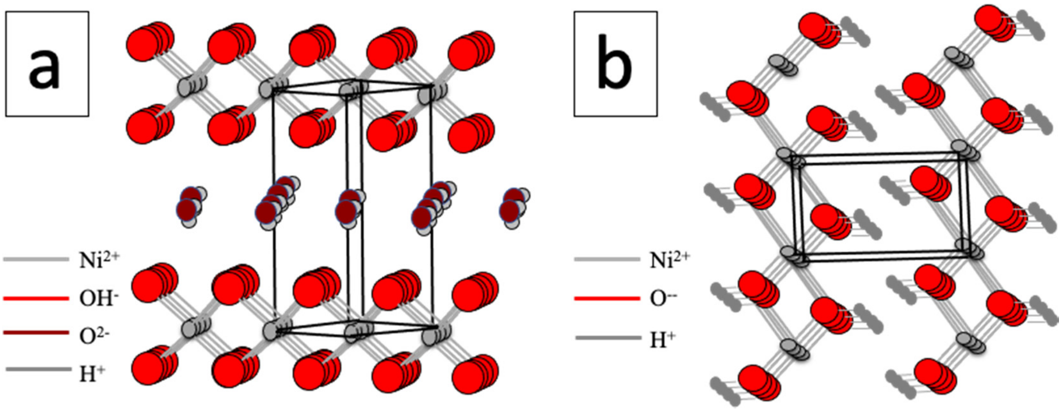

Figure 2: The structure of α-$Ni(OH)_2$ (a) and β-$Ni(OH)_2$ (b).

$$[6\mathrm{NiOOH}\cdot \mathrm{CO(NH_2)_2}]_{\mathrm{ads}} + \mathrm{H_2O} \rightarrow 6\mathrm{Ni(OH)_2} + \mathrm{N_2} + \mathrm{CO_2} \tag{19}$$

$$[\mathrm{NiOOH}\cdot \mathrm{CO(NH_2)_2}]_{\mathrm{ads}} + 6\mathrm{OH^-} \rightarrow [\mathrm{NiOOH}\cdot \mathrm{CO_2}]_{\mathrm{ads}} + \mathrm{N_2} + 5\mathrm{H_2O} + 6e^-, \tag{20}$$

$$\mathrm{NiOOH} + \mathrm{OH^-} \rightarrow [\mathrm{NiOOH}\cdot \mathrm{OH}]_{\mathrm{ads}} + e^-, \tag{21}$$

$$[\mathrm{NiOOH}\cdot \mathrm{CO_2}]_{\mathrm{ads}} + 2[\mathrm{NiOOH}\cdot \mathrm{OH}]_{\mathrm{ads}} \rightarrow 3\mathrm{NiOOH} + \mathrm{CO_3^{2-}} + \mathrm{H_2O}, \tag{22}$$

$$[\mathrm{NiOOH}\cdot \mathrm{CO_2}]_{\mathrm{ads}} + 2[\mathrm{OH^-}]_{\mathrm{sol}} \rightarrow \mathrm{NiOOH} + \mathrm{CO_3^{2-}} + \mathrm{H_2O}, \tag{23}$$

According to the above reactions, $Ni(OH)_2$ will be initially oxidized to NiOOH. The OH^- then deprotonates the amine group in urea. The remaining N will later be desorbed while transferring the electrons to the electrode. The adsorbed CO_2 will be discarded by hydroxides [43].

The mechanism of urea decomposition via electro-oxidation was studied by Botte et al. using DFT calculation [44]. The most possible mechanisms were set up by the electrophilic atoms of urea which interacted with the nucleophilic atoms of NiOOH and reversed. NiOOH as the active catalyst is formed by the interaction of Ni atoms with N and O in urea, while the bridging O interacts with the C atom in urea [36].

The electro-oxidation process of urea can also be explained using cyclic voltammetry. Vedharathinam and Botte reported the cyclic voltammogram urea electro-oxidation at Ni electrode in 5 M KOH with and without the presence of urea [1]. The cyclic voltammogram (Figure 3a) shows that in the absence of urea, a redox peak appears in the anodic and cathodic regions at 387 and 260 mV, respectively, implying the redox reaction of Ni^{2+}/Ni^{3+}. When urea is added to the electrolyte solution, an increase in current density is observed at the oxidation potential around 0.35 V (vs Hg/HgO), implying that the urea electro-oxidation has occurred on the surface of Ni electrode. Yan et al. also reported the same phenomena of urea electro-oxidation process in Ni–Co hydroxides electrode as shown in the cyclic voltammograms of Ni–Co hydroxides electrodes in the same condition as the previous one (Figure 3b) [35]. The oxidation peak is observed at the potential of 0.42 V indicating the formation of NiOOH from $Ni(OH)_2$. In the presents of urea, a strong oxidation current starts at 0.40 V was observed. This potential is similar to the potential formation of NiOOH, indicating that NiOOH is the active form of catalyst for the oxidation of urea. Table 1 shows the activity of various anode catalysts toward urea electro-oxidation.

2.3 Effect of KOH concentration

The use of KOH as the electrolyte in electrochemical oxidation of urea is reported to provide a better performance, in regards to the lower onset potential and the higher current density, than LiOH and NaOH [45] with the activity of urea oxidation of LiOH < NaOH < KOH. The surface poisoning effect of $PtOH–M^+ (H_2O)_x$ at the interface decreases the hydration energy of the alkali metal and further inhibits the active sites in the order of $Li^+ > Na^+ > K^+$ [46]. The increase in KOH concentration has been reported to improve the urea oxidation current density. As the KOH concentration increases, the OH^- which has a strong impact on the NiOOH development will lead to a decrease (shift to negative) in the onset

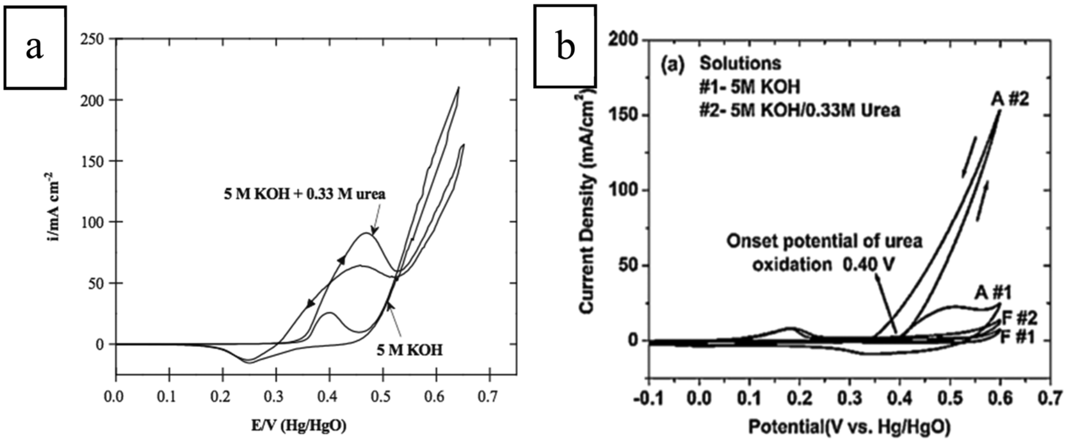

Figure 3: CVs of nickel nanoparticle electrode [1] (a) and Ni–Co hydroxide electrodes [35] (b) in 5 M KOH in the presence and absence of urea, republished with permission.

Table 1: Activity of various anode catalysts toward urea electro-oxidation

Anode catalysts	Preparation methods	Electrolytes	Onset potential	Anodic peak	Current density, mA cm^{-2}	Ref.
Single Ni metal catalyst						
Ni NPs/Ti rod	Electrodeposition	0.33 M urea in 5 M KOH	0.35 V vs Hg/HgO	0.46 V vs Hg/HgO	~90	[1]
Ni@carbon sponge	Electrodeposition	0.1 M urea in 1 M NaOH	0.35 V vs Ag/AgCl	0.52 V vs Ag/AgCl	~200	[50]
Ni-decorated graphene	Calcination	2.0 M urea in 1 M KOH	0.32 V vs Ag/AgCl	~0.8 V vs Ag/AgCl	~145	[51]
Ni/rGO	Aqueous-based reduction method	0.33 M urea in 1 M KOH	0.486 V vs MMO	0.65 V vs MMO	6.18	[52]
Ni Np/commercial carbon paper	Pulsed laser deposition	0.33 M urea + 1 M KOH	~0.425 V vs Hg/HgO	—	~4.8	[53]
Ni@GO	Chemical reduction	0.33 M + 1 M KOH	0.30 V vs SCE	0.49 V vs SCE	17.1	[54]
Ni–WC/C	Sequential impregnation method	0.33 M urea + 1 M KOH	0.4 V vs Hg/HgO	~0.55 V vs Hg/HgO	682 mg^{-1}	[55]
Ni–WC/MWCNT	Impregnation	0.33 M urea in 1 M KOH	~0.45 V vs Hg/HgO	~0.57 V vs Hg/HgO	46.6	[56]
CB/ads-Ni	Electrochemical deposition	0.33 M + 1 M KOH	0.45 V vs Hg/HgO	—	13	[57]
Nickel oxides and hydroxides						
β-$Ni(OH)_2$-CNTs	Facile hydrothermal reaction	0.33 M urea + 1 M KOH	0.32 V vs SCE	~0.55 V vs SCE	98.5	[58]
NiCo LDH/$NiCo(OH)_2$	Solution methods at room temp.	0.33 M urea + 5 M KOH	0.29 V vs Hg/HgO	—	~360	[59]
NiO/Gr-200 – carbon electrode	Precipitation step followed by calcination	0.3 M urea + 0.5 M KOH	0.36 V vs Ag/AgCl	0.51 V vs Ag/AgCl	30.94	[60]
NiO/Graphite	Chemical precipitation	0.3 M urea + 0.5 M KOH	0.345 V vs Ag/AgCl	0.64 V vs Ag/AgCl	17.63	[34]
NiO_x/GC	Electrodeposition	0.2 M urea + 0.5 M NaOH	~0.375 V vs SCE	0.47 V vs SCE	0.25	[33]
Ni–NiO/Gr-450	Annealing	0.33 M urea + 1 M KOH	~0.285 V vs SCE	0.5 V vs SCE	38.24	[61]
Ultrafine-NiO nanoparticles/GC	Electrodeposition	0.25 M urea + 1 M KOH	~0.35 V vs Ag/AgCl	0.47 V vs Ag/AgCl	15.34	[62]
NiO/NF	Chemical bath deposition	0.1 M urea + 8 M KOH	~0.3 V vs Ag/AgCl	0.48 V vs Ag/AgCl	222	[63]
Ni with other metals						
Ni–Co hydroxide/Ti foil	Electrodeposition	0.33 M urea in 5 M KOH	0.40 V vs Hg/HgO	—	~160	[35]
NiCo/carbon cloth	Hydrothermal	0.33 M urea in 1 M KOH	0.44 V vs Hg/HgO	~0.6 V vs Hg/HgO	~20	[64]
Ni–Co NWAs	Galvanostatic electrodeposition	0.33 M urea in 5 M KOH	0.19 V vs Ag/AgCl	0.6 V vs Ag/AgCl	380	[30]
Ni–Zn–Co/Ti foil	Electrodeposition, alkaline leaching	0.33 M urea in 5 M KOH	0.35 V vs Hg/HgO	0.5 V vs Hg/HgO	24	[65]
Ni–Co/MWCNT-AG	Polyol-reduction	1 M urea in 1 M KOH	0.302 V vs Ag/AgCl	~0.65 V vs Ag/AgCl	~120	[47]

(*Continued*)

Table 1: *Continued*

Anode catalysts	Preparation methods	Electrolytes	Onset potential	Anodic peak	Current density, mA cm^{-2}	Ref.
Ni–Cu/MWCNT	Two-step hydrothermal	0.07 M urea in 0.4 M KOH	~0.33 V vs Ag/AgCl	0.38 V vs Ag/AgCl	24.903	[66]
Ni–Cu/ZnO@MWCNT			~0.29 V vs Ag/AgCl	0.38 V vs Ag/AgCl	30.02	
Co–Ni@Nifoam	Facile dip and dry method, electroreduction, and electrodeposition methods	0.33 M urea in 5 M KOH	0.18 V vs Ag/AgCl	0.6 V vs Ag/AgCl	330	[67]
Co–Ni/rGO@Ni foam			0.14 V vs Ag/AgCl	0.6 V vs Ag/AgCl	223	
$Mn_{0.5}Ni_{2.0}Fe_{0.5}$/rGO	One-pot hydrothermal	0.33 M urea + 1 M KOH	~0.35 V vs Ag/AgCl	~0.45 V vs Ag/AgCl	1,750 mg^{-1}	[68]
Ni–Pd(P)/MWCNT	Hydrothermal methods	1 M urea + 3 M KOH	0.25 V vs Ag/AgCl	0.45 V vs Ag/AgCl	1897.76	[69]
FeNi oxide	Hydrothermal methods	0.33 M urea in 1 M KOH	0.265 V vs Ag/AgCl	—	36	[70]
$Ni_{0.8}Co_{0.2}(OH)_2$	Sol–gel method	0.2 M urea in 1 M KOH	0.25 V vs Ag/AgCl	~0.65 V vs Ag/AgCl	222	[71]
$NiWO_4$ NPs/rGO	Single step hydrothermal methods	0.33 urea + 1 M KOH	~0.3 V vs Ag/AgCl	0.428 V vs Ag/AgCl	218.1	[72]
Ni with specific morphologies						
NiO nanowalls/Ni foam	Hydrothermal methods	0.33 M urea + 1 M KOH	~0.4 V vs Hg/HgO	—	~1,000	[73]
Nanosheet $Ni(OH)_2$/Ni foam	Template-free growth	0.6 M urea in 5 M KOH	0.21 V vs Ag/AgCl	0.56 V vs Ag/AgCl	559	[74]
Nanoflakes nickel phosphates (Ni–P)	Reflux-based methods	1 M urea + 1 M KOH	0.345 V vs Ag/AgCl	0.45 V vs Ag/AgCl	20.55	[75]

SCE: standard calomel electrode.

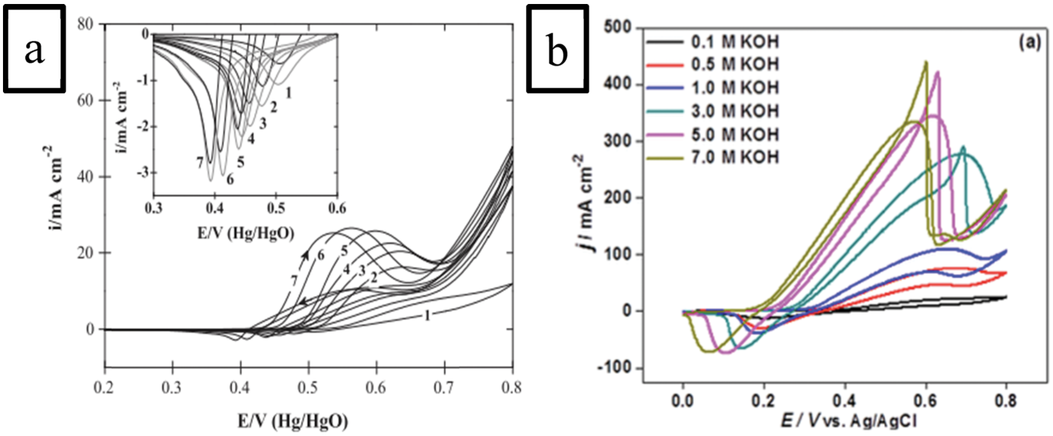

Figure 4: The dependence of urea electro-oxidation on KOH concentrations at (a) nickel nanoparticles and (b) NiCo/MWCNT electrodes. Scan rates of 10 and 20 mV s^{-1} were applied at (a) and (b), respectively, republished with permission [1,47].

potential of urea oxidation and concurrently increase the current density [1,47]. Figure 4 shows the CV curves using different KOH concentrations. The CVs imply that the current density keeps increasing until it reaches 5 M KOH, and then remains constant afterwards. It might be due to a full coverage of OH$^-$ on the catalyst that will lead to the blocking of the urea oxidation reaction [1]. Moreover, using a very high concentration of KOH will produce oxygen evolution reaction, catalyst oxidation, and accumulation of undesirable products [47].

2.4 Effect of urea concentration

Besides varying the KOH concentration, the urea concentration has also been investigated. CVs of Ni nanoparticle (NP) electrode [1] and NiCo/multi-walled carbon nanotube (MWCNT) [47] using different concentrations of urea is shown in Figure 5. It is shown that the increase in urea concentration leads to the increase in oxidation peak of urea. It might be because of the available urea for the oxidation reaction. In Figure 5a, the oxidation peak keeps increasing until it reaches 0.2 M urea. It was reported that after the concentration reaches above 0.2 M, the current density decreases due to a kinetics limitation because the catalyst surface is covered with urea molecules which decreases the urea oxidation rate due to the deprivation of OH$^-$ [1]. Meanwhile, in Figure 5b, the oxidation peak of urea keeps increasing until it reaches 1 M urea. After it surpasses 1 M, the oxidation peak decreases. The excess of urea will cover the catalyst surface and the reaction product will inhibit the contact with OH$^-$ to form NiOOH [47]. The maximum oxidation peak might be achieved by using different

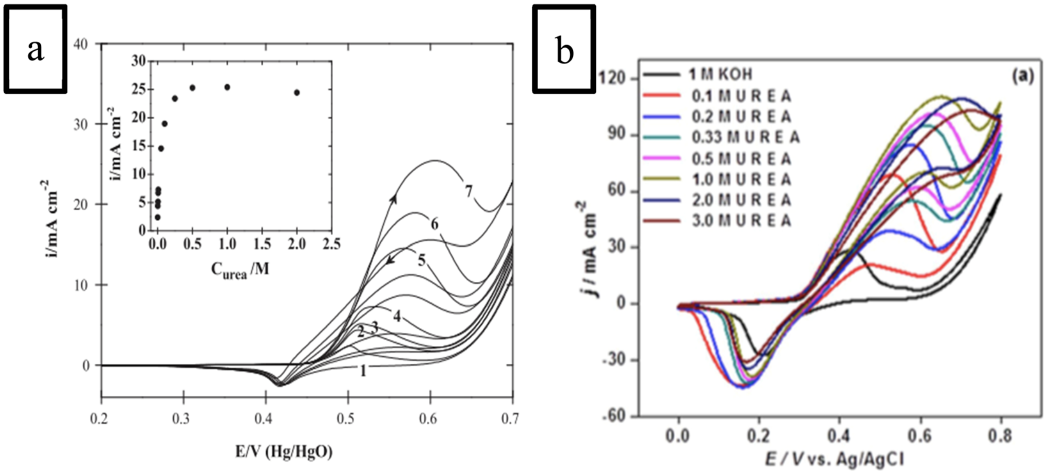

Figure 5: The dependence of urea electro-oxidation on urea concentrations at (a) nickel nanoparticle and (b) NiCo/MWCNT electrode. Scan rates at (a) was 10 mV s^{-1}, while at (b) was 20 mV s^{-1}, republished with permission [1,47].

KOH concentrations in different types of catalyst. Therefore, the optimization of urea is prescribed to achieve higher activity in DUFC.

3 Progress of anode catalyst for DUFC

The use of anode catalyst in DUFC has a great impact on the result of higher power density and it will improve the electrical performance of DUFC. There are many ways to improve the output of DUFC, namely by increasing the surface active sites of the catalyst, increasing the theoretical open circuit voltage (OCV) by using oxidants, and the most important way is by developing the anode catalyst of DUFC. Originally, noble metal catalyst has been used as the anode catalyst in DUFC, such as Ti/Pt, Ti/(Pt–Ir), and Ti/RuO_2 [48], which resulted in an unsatisfactory effect on DUFC, yet required a very high cost. Alternatively, using an affordable non-noble metal catalyst as the anode catalyst in urea fuel cell is reported to produce a highly effective result in DUFC. Nickel, in the form of NiOOH, has been reported as an excellent catalyst for urea electro-oxidation and could further increase the electrical performance of DUFC. There are many ways to increase the activity of Ni, such as by developing various morphologies of Ni, using high surface area supporting catalyst, and alloying Ni with various metals.

3.1 Single nickel metal catalyst

Nickel in the form of NiOOH was proven to be a promising catalyst in urea electro-oxidation. Vedharathinam and Botte (2012) have successfully electrodeposited Ni on the surface of Ti (inert) rod [1]. The Ni electrode was then applied as the anode catalyst (working electrode) for urea electro-oxidation process. Cyclic voltammetry study was conducted and confirmed that Ni is an active catalyst for urea electro-oxidation. In 2011, Lan and Tao have successfully synthesized Ni NPs (nanosized Ni) using KBH_4 reduction methods with the primary particles around 5 nm, but in some area the particles were around 2–3 nm [49].

Figure 6 shows the SEM images of the nanosized Ni compared to the commercial Ni. Figure 6a and b shows the images of nanosized Ni which have particle size of around 0.2 µm, whereas the ~50 nm particles are still in observation. Meanwhile, as can be seen in Figure 6c and d, the commercial Ni has much larger particle size compared to nanosized Ni, around 4–10 µm. It was reported

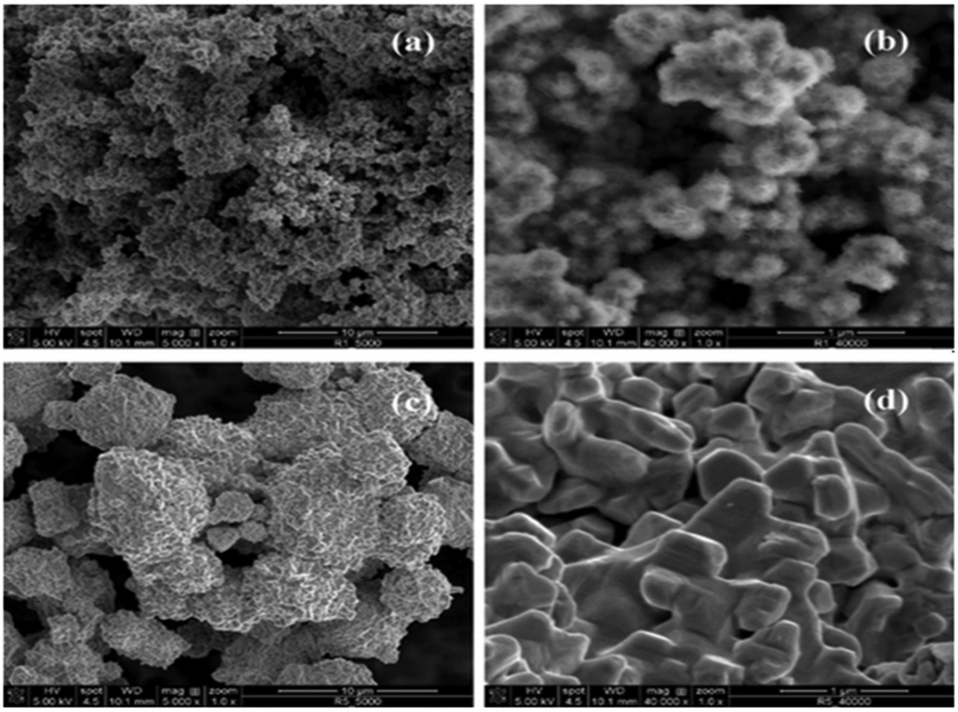

Figure 6: SEM characterization of nanosized nickel (a and b) and commercial nickel (c and d), republished with permission [49].

that nanosized Ni, which has a smaller size and larger surface area compared to the commercial Ni, shows a better performance in DUFC with a maximum power density of 14.2 mW cm^{-2} obtained at 60°C when using 1 M urea as fuel placed in anode chamber and humidified air was filled in the cathode chamber. The smaller size of the particles could lead to larger surface area which is an ideal condition of DUFC catalyst. This result indicates that nanosized Ni is a promising catalyst in urea electro-oxidation as well as DUFC.

3.2 Nickel hydroxides

As mentioned above, $Ni(OH)_2$ generally forms two types of crystals, namely α-$Ni(OH)_2$ and β-$Ni(OH)_2$ forms. In the α-$Ni(OH)_2$ form, intercalations between the layers by additional anions neutralize the positive layers with the spacing distributed between 7.5 and 31.7 Å and lead to higher electrochemical activity as the conductive layers could sustain the electrolyte transfer to the α-$Ni(OH)_2$ layer. Meanwhile, in the β-$Ni(OH)_2$ form, the layers are closely arranged which lead to minor interlayer spacing and affect the amount of electrolyte entering the layers of β-$Ni(OH)_2$, thus could lower the electrochemical activity [48].

To decrease the over-potential and obtain an optimum performance of DUFC, Wang et al. have modified glassy carbon electrodes with two-dimensional $Ni(OH)_2$ nanosheets [76]. XRD characterization confirmed the interlayer spacing of 2.67 nm, indicating that $Ni(OH)_2$ nanosheets have been deposited in the form of α-$Ni(OH)_2$. The electrochemical study conducted in KOH with the absence and the presence of urea confirmed that in the absence of urea, the current density increased to 154 mA cm^{-2} mg^{-1}. The α-$Ni(OH)_2$ form could lower the onset potential by 100 mV compared to the bulk $Ni(OH)_2$. In 2012, Wang et al. successfully synthesized nickel hydroxide nanoribbons through hydrothermal treatment. The XRD characterization confirmed the pattern of β-$Ni(OH)_2$ phase with the sample thickness of around 15–20 nm [77]. Electrochemical study conducted with the same previous condition, using KOH in the absence and the presence of urea, showed that nickel hydroxide nanoribbon enhanced the current density to 7 mA cm^{-2} mg^{-1}. Accordingly, it is confirmed that α-$Ni(OH)_2$ provided higher current density of urea electro-oxidation than the β-$Ni(OH)_2$.

In 2016, Ye et al. reported the use of $Ni(OH)_2$/Ni foam as the anode catalyst in DUFC. $Ni(OH)_2$/Ni foam was prepared in various morphologies, which are sheet-like (SH), flower-like (FL), nanosheet (NS), and twin-like (TW), to optimize the performance toward urea electro-oxidation [74]. All the configurations were then examined as anode catalyst. The result showed that NS $Ni(OH)_2$/Ni foam generated a higher current density of urea electro-oxidation compared to the other configurations of $Ni(OH)_2$/Ni foam. This is because the NS $Ni(OH)_2$/Ni foam morphology has a larger surface area than the other configurations. The SEM images of the prepared electrode in various morphologies (Figure 7a) show that SH $Ni(OH)_2$/Ni foam consists of thick sheets, while flower-like shape $Ni(OH)_2$ is well distributed in Ni foams. In regards to NS $Ni(OH)_2$/Ni foam, it is fully coated with nanosheet $Ni(OH)_2$. Meanwhile, compact film of $Ni(OH)_2$ is homogenously distributed on TL $Ni(OH)_2$/Ni foam. The comparison of all modified Ni foams toward urea electro-oxidation in alkaline medium (KOH) and their DUFC performances are displayed in Figure 7b and c, respectively. These figures imply that NS $Ni(OH)_2$/Ni foam has a loose structure with many open spaces which lead to a higher surface area, so it is sufficient for the electro-catalytic performance of DUFC.

3.3 Ni with other metals

Although Ni in the form of NiOOH has been proven as the promising catalyst towards urea electro-oxidation, the NiOOH itself has a high overpotential which could further decrease the result of DUFC. Likewise, the use of Ni catalyst is most likely to be fouling throughout the electro-oxidation process which could disband the NiOOH as the active site of the catalyst. Doped Ni with other metal has been reported to be able to improve the electrocatalytic activities and reduce the abovementioned difficulties. King et al. [78] reported the modification of Ni with noble metals, including Pt–Ni [79], Pt–Ir–Ni, Ru–Ni, Pd [80], and Rh–Ni [78]. Between all the various combinations, the combination of Rh and Ni could create a synergistic effect because it has been proven to lower the overpotential and increase the stability in the urea electro-oxidation. Electrochemical study of Rh–Ni electrode with 0.33 M urea in 1 M KOH as the electrolyte is reported to achieve the current density of ~80 mA cm^{-2} during the cyclic voltammetry. In 2012, Miller et al. have reported to use Rh/Ni electrodes, which were developed by depositing Rh on Ni foil using constant potential techniques [81]. It was reported that the addition of Rh lead to an increase in current density, which implied the role of Rh in the oxidation acceleration of $Ni(OH)_2$ to NiOOH. Alloying of Ni-Rh occurs when Rh is deposited on the

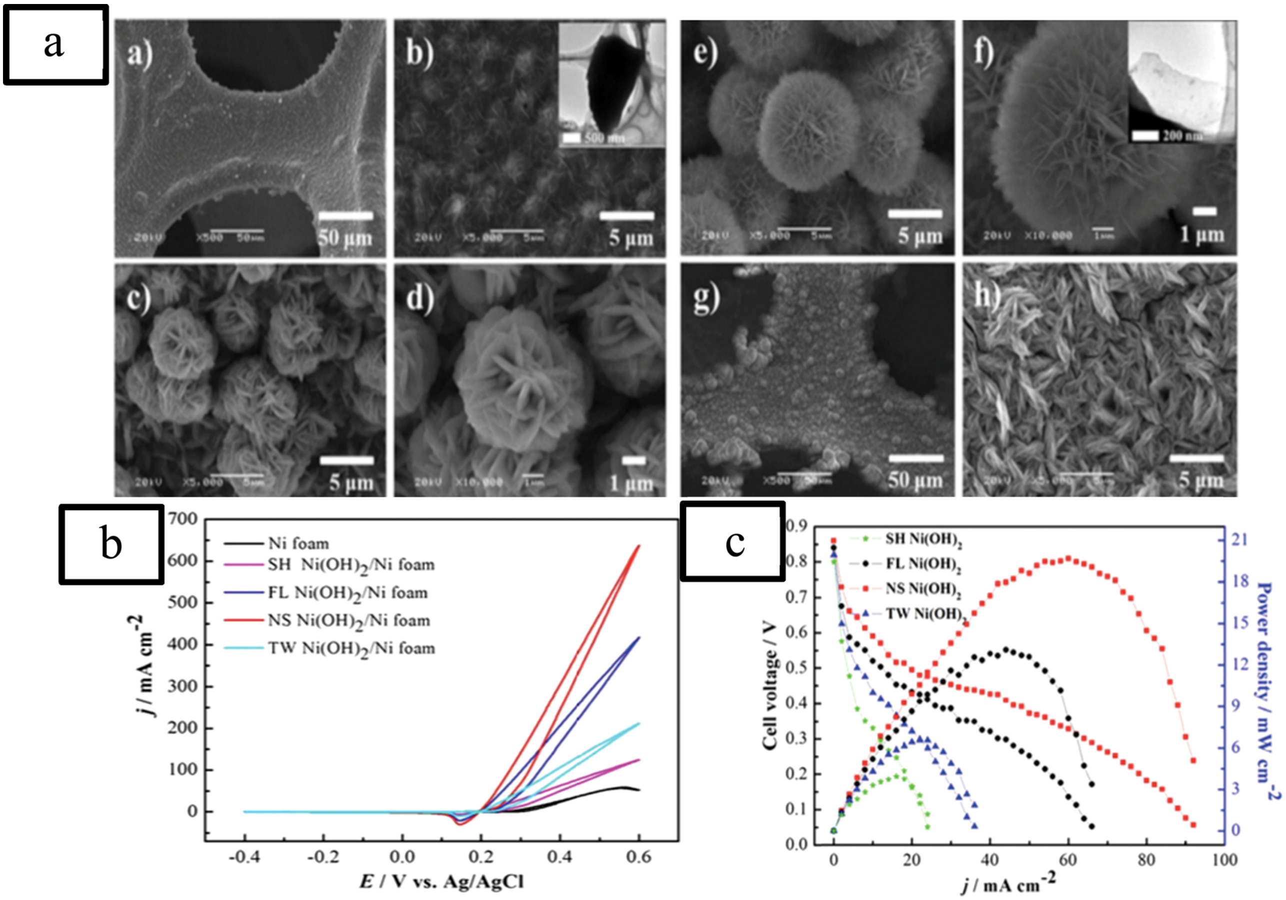

Figure 7: SEM visualization of sheet-like ((a and b); flower like (c and d); nanosheets (e and f); and twin-like (g and h)) (a); the CVs of various morphologies of $Ni(OH)_2$/Ni foams (b) and the DUFC performances using all morphologies (c), republished with permission of Royal Society of Chemistry, from [74]; permission conveyed through Copyright Clearance Center, Inc.

surface of Ni at lower potential; however, the best catalytic performance occurs when Rh is not alloyed with Ni, which means that only monometallic Rh is deposited on the Ni surface.

Alloying Ni with noble metal catalyst has been proven to increase the effectivity toward urea electro-oxidation, but the high cost of the noble metal catalyst remains as the main problem if this will be further used in a larger scale application. Therefore, doping or alloying Ni with non-noble metal catalyst is one way to overcome this problem. Alloying or doping non-noble metal catalyst, such as Co [71], Mn [82], Zn [65], Fe [83], Cr [84], Mo [85], etc., to Ni has been proven to decrease the onset potential of NiOOH and improve the catalytic activity toward urea electro-oxidation in DUFC application. Cobalt has been widely used to decrease the onset potential of NiOOH formation to further optimize the electrocatalytic activity toward urea electro-oxidation. Wei et al. (2011) used Ni–Co bimetallic hydroxide film deposited on Ti foil as the anode catalyst for urea electro-oxidation. It was reported that alloying Ni and Co produced a significant reduction in the overpotential of NiOOH (it decreases at about 150 mV) when compared with only nickel hydroxide electrode [35]. In 2014, Xu et al. also reported the use of nickel–cobalt bimetallic (NiCo/C) for the anode catalyst for DUFC [64]. A reduction method using $NaBH_4$ was applied to prepare NiCo/C with various Co ratios to optimize the use of Co. An average particle size of NiCo NPs is calculated to be around 30–40 nm. The most negative potential is obtained using Ni_3Co_2/C, indicating that the use of Co could lower the onset potential. On the other hand, the increase in Co content decreases the electro-oxidation current of urea because of the inactive activity of Co urea electro-oxidation. Therefore, it is important to control the balance of Ni and Co ratio to obtain higher catalytic activity. A maximum power density of 1.57 mW cm^{-2} could be achieved at NiCo/C electrode using 0.33 M urea as the fuel and O_2 as the oxidant, which were filled in the anode and cathode chambers, respectively, at 60°C. Yan et al. reported that the use of Zn and Co as the multi-metal catalyst in Ni could enhance the catalytic activity toward electro-oxidation, since Co itself is inactive [65]. It was reported that using Ni–Zn as the metal catalyst decreases the onset potential from 0.43 to 0.39 V, while using Ni–Zn–Co it decreases the onset potential to 0.35 V. The higher current density is achieved using Ni–Zn–Co as the anode catalyst of urea electro-oxidation. Mn is used to help remove the poisonous intermediates formed on the catalyst surfaces. Mn also helps to reduce the overpotential of NiOOH formation. In 2016, Barakat et al. used NiMn NPs-decorated carbon nanofibers (NiMn-CNFs) as the anode catalyst for urea electro-oxidation [86]. It was reported that NiMn-CNFs show a better electrocatalytic activity toward urea oxidation compared to Ni-CNFs, which is almost three times higher. In 2017, Singh and Schechter alloyed Ni with Cr which resulted in an increase in the electro-oxidation activity of urea and shifting the redox peak to the more negative potentials [87]. Using NiCr/C results in higher current density than that obtained by using Ni/C, which is 3.6 times higher.

3.4 Ni with specific morphologies

Besides optimizing the anode catalyst in the form of Ni metal, nickel hydroxides, and alloying Ni with other metals, the morphologies are also considered to enhance the surface area which later could enhance the electrical performance of DUFC. Many morphologies have been successfully developed, such as nanowires, nanofibers, nanosheet, and many more.

In 2014, Yan et al. fabricated two various Ni structures, i.e., nickel nanowire electrocatalyst (NNE) and nickel film electrocatalyst (NFE), using electrodeposition technique at an applied potential of −0.85 V vs Ag/AgCl [88]. Anodic aluminum oxide (AAO) template was used to fabricate the NNE. The deposition time for NNE was 60 min and that for NFE was only 6 min. Both NNE and NFE obtained the same loading Ni. Figure 8a shows the SEM characterization of both nickel nanowire electrodes in the form of NFE and NNE. It is also shown in the electrochemical studies of urea electro-oxidation using CVs (Figure 8b) which reveals that NNE has achieved higher electrocatalytic activity and higher current density compared to NFE. It is mainly because there is no assistance of AAO resulting in nickel particle with partial agglomeration; meanwhile, the use of AAO template resulted in a larger surface area with an average diameter of 90 nm and electro-active surface area of 79.1 $cm^2\ mg^{-1}$. It is also reported that the current density of 40 $mA\ cm^{-2}$ at 0.55 V (vs Hg/HgO) could be achieved when using NNE. In 2014, Guo et al. have successfully prepared fully metallic structure of nickel nanowire array (NWA) electrode developed by doping the Ni particles within the pores through electrodeposition methods and over-plating it on the surface of polycarbonate template (Guo et al., 2016). The prepared NWAs have an active surface area of 25.21 cm^2 and 50 nm diameter for a single wire. Comparison of NWAs with a flat Ni electrode showed the noticeable decrease in the onset potential of urea electro-oxidation with a higher peak current density, indicating that the nanowire array structure is promising for anode catalyst application in DUFC.

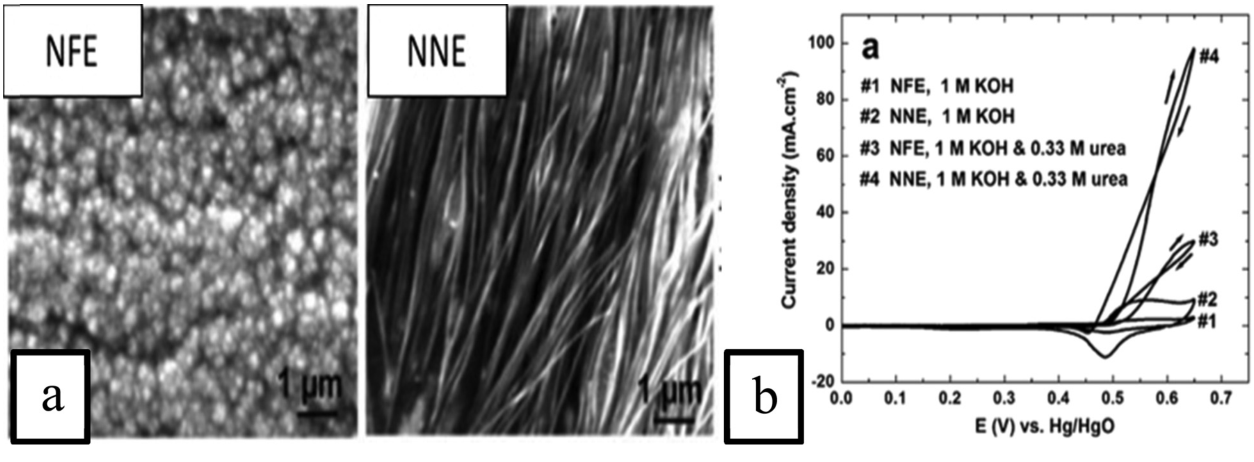

Figure 8: SEM characterization of nickel nanowires in the form of NFE and NNE (a) and the CVs of nickel nanowires with different form in 1 M KOH in the presence and absence of 0.33 M urea (b), republished with permission [89].

4 DUFC performances

DUFC has been considered as a promising alternative for the renewable energy due to the use of wastes which could generate electricity with high efficiency. Compared to the PEMFC, which uses hydrogen as the energy resources, DUFC has an excellence factor such as the use of urea-containing wastewater. Hydrogen, which is a clean energy, still has many drawbacks such as its difficult production, storage, and the transportation and will create difficulties in the process to make it a large-scale application [89]. DUFC, on the other hand, using urea as the energy sources leads to an easy-storage and easy-transport, non-toxic, and could make use of the high amount of urea-containing wastewater found in human and animal urine and industrial area [90]. The urea electro-oxidation process is the primary key to generate high electricity. Therefore, the current progress of anode catalyst to improve the catalytic activity in urea electro-oxidation is investigated.

Basically, the instrument used in DUFC is the same as the conventional fuel cell. DUFC is often used in two-chamber cell which contains the anode chamber and cathode chamber. An ion exchange membrane is placed between the two chambers [91,92]. In each chamber, there are catalysts which will act as the working electrode and the counter electrode. Generally, the flow cell is used to perform the DUFC application.

Already in 1973, Yao et al. conducted an experiment to generate electricity using urea as the energy source by using Pt as the catalyst in the trial [31]. The experiments result presented evidence that oxidation of urea transforms into CO_2, N_2, and H_2O using Pt as the anode and cathode catalysts. The investigation of first DUFC was reported by Lan et al. in 2010 which compared the use of Pt/C and Ni/C as the anodes. The use of Pt/C electrodes as both cathode and anode catalysts produced the OCV of 0.5 V and the power density of 0.2 $mW\,cm^{-2}$ at room temperature. Meanwhile, when using Ni/C as the anode and Ag/C-MnO_2/C as the cathode, an anion-exchange resin-PVA membrane was utilized due to the use of basic electrolyte in the anode chamber. This system resulted in a maximum power density of 1.7 $mW\,cm^{-2}$ at 50°C. This work proves that DUFC could be executed using Ni as a non-noble metal catalyst. Afterwards, the recent progress of anode catalyst has been investigated. In 2014, Xu et al. used nickel–cobalt bimetallic/C (NiCo/C) as the anode catalyst. It was proven that the Co doping could reduce the overpotential of Ni toward urea-oxidation and further improve the catalytic activity [64]. Application using 0.33 M urea as a fuel (anode electrolyte) and O_2 which was filled in the cathode chamber at 60°C temperature generated a maximum power density of 1.57 $mW\,cm^{-2}$, while the use of urine as the fuel achieved a maximum power density of 0.19 $mW\,cm^{-2}$ and OCV of 0.38 V at 60°C. In 2016, the use of nickel–cobalt nanowire arrays (Ni–Co NWAs) as the anode catalyst in DUFC produced a maximum OCV and power density of 0.92 V and 7.4 $mW\,cm^{-2}$, respectively, at room temperature [30]. In this DUFC, a solution of 0.33 M urea in 9 M KOH was used as the anode electrolyte and a solution containing 2 M H_2O_2 and 2 M H_2SO_4 was placed as the cathode electrolyte. It was also confirmed that this type of DUFC showed a good stability during one-hour durability test. Basumatary et al. reported Ni-Cu/ZnO@MWCNT application as anode catalyst could enhance the surface area and improve the catalytic activity and further enhance the electricity performance of DUFC to be higher [66]. Maximum power density of 26.9 and 44.36 $mW\,cm^{-2}$ were achieved at 20 and 50°C, respectively, using 3 M KOH/0.7 M urea as the anode electrolyte. This result was the highest output of power density reported at 50°C. Ranjani et al. developed 3D hierarchical nickel cobaltite ($NiCo_2O_4$) on carbon cloth (CC) fibers as anode catalyst in DUFC [93]. It was reported that maximum power density of 38 $mW\,cm^{-2}$ could be generated using 50 mM urea in 0.1 M KOH at 80°C (Figure 9a). Higher result could not be accomplished due to the synergistic impact of Ni^{2+} ion which substituted in the octahedral sites of Co_3O_4 and the 3D hierarchical configuration which leads to limiting the oxygen evolution reaction and further improves the urea electro-oxidation reaction. Besides, the use of this anode catalyst could achieve 180 h durability test due to its large surface area (Figure 9b).

Besides the optimization of anode catalyst, the use of high surface area supporting electrode of the anode catalyst could also determine the performances. The use of ion exchange membrane and the use of cathodic oxidants were also reported to have an impact on the electrical performances of DUFC.

4.1 Supporting electrode

One of the main reasons for higher electrical performances is the surface area of the catalyst, both in the anode and cathode chambers. Commonly, C has been used as the supporting electrode due to its inexpensive material, such as graphene [41,58], CNTs [47,94], and CNFs [86]. Additionally, boron-doped diamond [95], Ni foam [63], and many more were also reported.

Li et al. have reported the use of CoNi nanosheet array which was grown in Ni foam modified by reducing

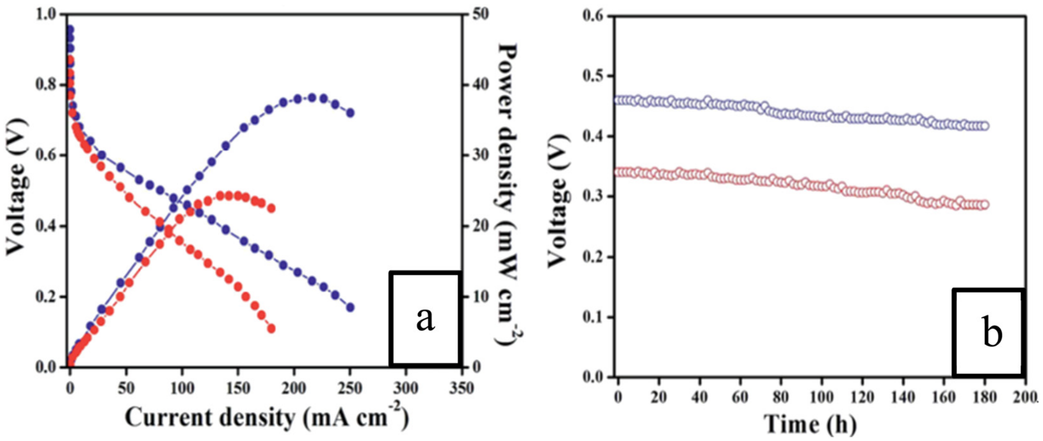

Figure 9: DUFC performance of $NiCo_2O_4$/CC using urea (blue line) and human urine (red line) at 80°C (a), and durability test of $NiCo_2O_4$/CC in urea (blue line) and human urine (red line) for 180 h at 80°C (b), republished with permission of Royal Society of Chemistry, from ref. [94]; permission conveyed through Copyright Clearance Center, Inc.

graphene oxide (rGO) as the anode catalyst in DUFC [67]. The GO was attached to Ni foam through facile dip and dry method and further reduced to reducing graphene oxide by electroreduction method. The distribution of CoNi nanosheet arrays in the rGO/Ni foam contributes to the increase in the surface area. Ni foam was selected as the supporting electrode due to its large surface area, whereas the modification using rGO produces a more larger surface area CoNi/rGO/Ni foam electrode. This electrode successfully formed a porous surface electrode that provides abundant active sites on the catalyst to enhance the urea oxidation performance. A good stability for 1 h application time was also demonstrated. This implies a good stability for 1 h, although longer stability test still needs to be conducted to evaluate the catalyst durability for daily or even industrial use in the future. Basumatary et al. also reported the use of Ni–Cu alloy NPs which was deposited onto the surface of ZnO-coated MWCNTs [66]. The Ni–Cu/ZnO@MWCNTs was prepared using a two-step hydrothermal process. MWCNTs are usually used as supporting electrodes in DUFC due to its large surface area and good thermal and chemical stability in acidic and base media. However, to uniformly distribute metal NP onto the surface of MWCNTs is rather difficult. To solve this problem, ZnO was coated onto the MWCNTs to achieve high distribution of metal NPs as well as to increase the catalytic activity of the catalysts. It is reported that uniform distribution of Ni–Cu NPs on the entire surface of ZnO@MWCNT was successfully performed without agglomeration as also confirmed by the TEM characterization. The average particle size of Ni–Cu NPs of around 2.5 ± 0.31 nm was observed. The result implied that the use of ZnO@MWCNT as the supporting electrode enlarged the surface area and accordingly increased the catalytic activity of the catalyst as well as the electrical performance of DUFC. However, as the stability test has not been reported in this work, hence review of the stability and durability performance of this electrode could not be performed.

The above two examples showed that the use of supporting electrode is greatly important to form larger surface area and escalate the urea oxidation performance. Furthermore, it is also crucial to observe the stability and durability of the electrodes for suitable and repetitive use, especially for daily use and in industrial scale.

4.2 Cathode electrolyte: using H_2O_2 as oxidants

In DUFC, oxygen (air) commonly has been used as the cathode electrolyte. However, it has been reported that replacing oxygen with oxidants could help to improve the electrical performances of DUFC due to its theoretical cathodic potential, which is twice as high as the oxygen. Besides, the use of oxidants is proven to create a faster electro-reduction kinetics [96]. As mentioned above, the theoretical cathodic potential increases from 0.40 V vs SHE, when O_2 is applied as the cathode electrolyte, to 1.763 V vs SHE, when H_2O_2 is applied as the cathode electrolyte. It increases the potential around 0.87 V vs SHE. Another advantage in using H_2O_2 is that oxygen density in liquid phase is around a thousand times higher than in its gaseous phase. Thus, it will enhance a higher current density in the DUFC application [27].

In 2014, Xu et al. have used bimetallic Ni–Co deposited on carbon cloth as an anode catalyst in DUFC [64].

0.33 M urea has been delivered into flow channels and used as the fuel (anode electrolyte), while humidification oxygen has been used as the cathode electrolyte. Maximum power density of 1.57 mW cm^{-2} is obtained at a temperature of 60°C. Serban et al. in 2014 was the first to introduce the use of H_2O_2 as the cathode electrolyte for DUFC application [27]. It was reported that the use of Ni/MWCNTs can produce a maximum power density of 0.05 mW cm^{-2}, when using a solution containing 1 M urea and 1.5 M NaOH as an anode electrolyte and a solution containing 20% H_2O_2 and 5% H_3PO_4 as the cathode electrolyte [27]. Since then, the use of H_2O_2 as the cathode electrolyte for DUFC application has gained great attentions and further optimized. In 2016, Guo et al. used porous Ni–Co anode catalyst for DUFC application with a solution containing 0.5 M urea and 7 M KOH as the anode electrolyte and a solution containing 2 M H_2O_2 and 2 M H_2SO_4 as the cathode electrolyte. Applications at 20 and 70°C was reported to produce the maximum power density of 17.4 and 31.5 mW cm^{-2}, respectively [97]. Compared to the use of O_2 as the cathodic oxidants, the use of H_2O_2 is proven to produce higher electrical performance in DUFC application.

The difference in the cathodic oxidants leads to different exchange membrane used in the DUFC application. Typically, anion exchange membrane was used as the exchange membrane when O_2 was used as the cathodic oxidants. It was reported that ammonia (a weak base) will be produced during the hydrolysis of urea in this application, because of which the cation exchange membrane (commonly, Nafion) cannot be used since it is compatible in acidic medium. Therefore, anion exchange membrane is more suitable to be used in DUFC application when O_2 has a role of the cathodic oxidants [10]. In this type of DUFC, the OH^- produced in the cathode chamber will go over the anion exchange membrane into the anode chamber. The OH^- ions then further react with urea and release electrons which are transported over the external circuit and could determine the electrical performances [28]. The advantage of using anion exchange membrane is that it is an alkaline-based electrolyte which makes it compatible and enables it to provide the alkaline condition [98].

Meanwhile, when H_2O_2 is used as the cathodic oxidants, the cation exchange membrane (Nafion) is used as the exchange membrane. In this situation, K^+ produced from the reaction in the anode plays a role as the transport ion through the Nafion and goes into the cathode chamber and reacts with the SO_4^{2-} ions and forms K_2SO_4 [97].

5 Future challenges and perspective

The DUFC has been proven to be a promising alternative for the replacement of fossil fuel to produce electricity, although some optimization is still needed to achieve the optimum result. The very important part in this system is the catalysts, both in cathode and anode. Catalyst with a large surface area is desired to provide sufficient active sites, especially for the anode catalyst since it will have a direct contact toward urea as the fuel in this type of fuel cells. Thus, modification to obtain large surface area is highly desirable for anode catalyst in DUFC. Besides, the use of H_2O_2 cathode electrolyte has also been proven as one effective method to achieve higher electrical performances. However, H_2O_2 in acidic medium is needed to optimize the theoretical cell voltage. It means that two different conditions are needed in this type of DUFC, alkaline medium in the anode chamber and acidic medium in the cathode chamber. Therefore, the anode catalyst which has a good corrosion resistance is needed. The use of anion exchange membrane is also required to be maintained due to its stability issue and also its low anionic conductivities [99]. It is also very important to examine the catalysts performance toward urea electro-oxidation using electrochemical impedance spectroscopy [67]. It will give information about the resistance value of the catalyst system before being used as the anode catalyst in DUFC.

Besides its modification of Ni-based catalyst, which are desired to optimize the performance of DUFC, the stability test is also required to evaluate the performance so it could be employed for a daily use or industrial scale. Finally, this system also needs to be examined using the wastewater sample, such as human or animal urine and industrial waste. After the optimization of the importance factors mentioned above, this type of fuel cell could be applied as a promising replacement of the fossil fuel and become the effective devices for wastewater treatment and electricity production.

6 Conclusion

The purpose of this review is to report the recent progress in DUFC, specifically for the anode catalyst progress in DUFC. It can be concluded that DUFC is a greatly promising substitution for the fossil fuel. The use of wastewater that contains urea, which is further oxidized into N_2, CO_2, and H_2O, could help to generate electricity. Despite highly promising for application in DUFC, some important factors need to be optimized to produce an excellent performance. The optimization of anode catalyst is desired to achieve higher performances toward urea electro-oxidation. It is reported that Ni, a non-noble and low-cost metal catalyst, is a better catalyst for urea electro-oxidation compared to the noble metal catalyst, such as Pt. However, the formation potential of NiOOH, the active catalyst for urea electro-oxidation, is high. Therefore, doping Ni with other metals, such as Co, Mn, Zn, or Cr is needed. The morphologies of the catalyst are also reported to increase the catalytic performances due to the achieved larger surface area. Besides, using a supporting electrode with greater surface area, such as Ni foam, MWCNT, etc., is also important to improve the DUFC performances. It is very important to modify the anode catalyst to increase the surface area, so it could provide sufficient active sites between the catalyst and urea as the fuel. Moreover, it is also very crucial to optimize the electrolyte condition in this DUFC system, such as usage of H_2O_2 over O_2 as the cathodic oxidant in the cathode electrolyte, which theoretically produces higher cathodic potential and also optimizes the use of exchange membrane (cation or anion) to achieve a suitable environment in enhancing the performance of DUFC.

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Conflict of interest: There is no competing interest.

Ethical approval: The conducted research is not related to either human or animal use.

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